

*A Study of Catalytic Actions at Solid Surfaces. Part VIII.—
The Action of Sodium Carbonate in Promoting the Hydrogenation of Phenol.*

By E. F. ARMSTRONG, D.Sc., F.R.S., and T. P. HILDITCH, D.Sc.

(Received June 7, 1922.)

Although the action of poisons on catalysts resulting in retardation or prevention of chemical action is well understood, much mystery still attaches to the so-called promoters of catalytic action. There are now a large number of well authenticated cases, both in scientific and patent literature, in which the presence of another metal or of some salt or other substance along with the catalyst facilitates action. No general explanation of promoter action has been advanced though attempts have been made to explain special cases.

Rideal and Taylor,* dealing with the ammonia synthesis, consider that the "promoter" may alter the relative adsorption of the reacting substances so that the optimum ratio for the desired interaction is more nearly approached. Pease and Taylor† have given a useful summary of the literature on catalyst promoters, with a view rather to future systematic investigation than to the establishment of a general theory at the present stage. Bancroft‡ has suggested that, instead of changing the ratio of adsorption, the promoter activates one of the interacting bodies chiefly, whilst the catalytic agent activates the other, the activation consisting apparently in some rearrangement of the chemical forces in the activated molecule. Palmer§ has recently suggested that the accelerating action of small amounts of magnesia or manganese oxide on the dehydrogenating capacity of copper is connected with selective absorption in the infra-red region of the spectrum, the whole process being due to radiation.

Before seeking any general theory to explain so many diversified phenomena it appeared to us desirable to investigate certain specific instances, the more especially as it seemed probable that definite and simple chemical explanations would be found differing from case to case. This expectation has been fully realised in the examples which are the subject of this and the following papers, in which it is shown that the

* 'Catalysis in Theory and Practice,' pp. 29-31 (1919).

† 'J. Phys. Chem.,' vol. 24, p. 241 (1920).

‡ 'J. Ind. Eng. Chem.,' vol. 14, p. 331 (1922).

§ 'Roy. Soc. Proc.,' A, vol. 101, pp. 175-186 (1922).

activity of the promoter is due to causes which may be termed essentially chemical rather than physical. We would, however, at this stage of the enquiry specifically refrain from generalising on the subject.

We have made a prolonged study of the hydrogenation of liquid phenol in presence of nickel. This proceeds readily at 150–190° C., the products being cyclohexanol and cyclohexanone. The phenol must be very drastically purified before consistent results can be obtained, and even so, it is rarely found that two separate preparations of phenol are hydrogenated at exactly the same rate. In all cases, therefore, we have conducted a complete series of experiments on the same sample of purified phenol.

Few of the many workers on the hydrogenation of aromatic compounds seem to have studied the process kinetically, but Vavon and Detrie* state that in presence of platinum black a yield of 66 per cent. of cyclohexanol is produced, cyclohexanone being formed intermediately, and apparently an equilibrium is set up in which phenol is still present.

We find that, under the best conditions, little or no unchanged phenol is left, and that, by the time the phenol has all been transformed, the product consists of about 95 per cent. cyclohexanol and the remainder cyclohexanone.

Even with pure phenol, however, the action is notably accelerated by the presence of small quantities of mildly alkaline salts. Of those investigated, anhydrous sodium carbonate has proved the most suitable, whilst sodium borate acts similarly, but less energetically. The addition of caustic soda is detrimental, whilst anhydrous sodium phenate, sulphate or acetate produce a feeble acceleration by no means comparable with the effect of the carbonate. The presence of water retards the hydrogenation of liquid phenol, and the stimulation is only observed when the anhydrous salts are employed.

The following experiments illustrate the effect of varying proportions of sodium carbonate on the rate of hydrogenation of phenol. One hundred grams of pure phenol were taken for each experiment and hydrogenated at 180° C. for 1 hour under 80 lb. per square inch pressure of pure hydrogen, in presence of varying amounts of nickel and of sodium carbonate. The products were analysed and the percentage of reduction products isolated in each case is given in the following Table.

Thus sodium carbonate exerts an accelerating effect which is dependent on the amount present, the hydrogenation being retarded if an excess of the carbonate is present; moreover, the optimum amount of carbonate is not

* 'Compt. Rend.,' vol. 172, p. 1231 (1921).

given by any definite concentration with respect to the phenol, for it varies in each of the cases.

Nickel present	1·0 grm.	0·50 grm.	0·20 grm.
Sodium carbonate—			
Nil	84·0	74·4	50·0
0·025 grm.	—	—	70·5
0·050 , ,	90·7	89·3	94·7
0·075 , ,	—	—	74·2
0·100 , ,	94·3	93·0	76·1
0·125 , ,	—	96·3	
0·150 , ,	—	94·4	
0·200 , ,	100·0	88·8	42·9
0·400 , ,	100·0	69·4	31·1
0·600 , ,	89·3		

On the contrary, it is directly related to the amount of nickel present, as the following analysis of the preceding data shows:—

Weight of phenol.	Weight of nickel.	Optimum weight of carbonate.	Percentage Na_2CO_3 on nickel.
grm.	grm.	grm.	
100	1·0	0·2-0·4	20-40
100	0·5	0·1-0·15	20-30
100	0·2	0·05	25

Thus sodium carbonate exerts its maximum influence when present to the extent of about 25 per cent. of the weight of nickel used in each case. It should be observed that this is the proportion of sodium carbonate with respect to the whole of the metallic nickel present; the whole of this is not necessarily concerned in actual catalysis, as we have shown in a previous paper,* but on the other hand, since the same preparation of catalyst was used throughout each series, the proportion of active nickel present will be proportional to the total weight used in each case.

The mechanism by which the sodium carbonate assists the process has not been discovered. It is possible that in some way the carbonate is associated with the catalyst, and protects it against the acidic influence of the phenol. However this may be, there is no measurable amount of carbonate associated with the nickel at the close of the experiment; the filtered residue of catalyst has been examined and found to be practically free from sodium carbonate, which must therefore be distributed in the liquid product of the action. Furthermore, sodium carbonate has been found to have a deleterious effect

* Part VI of this series, 'Roy. Soc. Proc.', A, vol. 99, p. 494 (1921).

when added during the hydrogenation of organic acids, the stimulating action having only been observed, so far, amongst phenols (phenol, *o*-, *m*-, and *p*-cresol, β -naphthol, and thymol).

Whilst the precise action of the carbonate is thus still obscure, we have clear evidence to show that the stimulation produced is not a true acceleration, but the restoration of the nickel to its normal function by the suppression of a retardation. This is shown by a comparison of the mean rates of absorption of hydrogen (litres per minute) over successive 10-litre periods, when 100 grm. of phenol were hydrogenated in presence of 0.5 grm. of nickel and varying proportions of sodium carbonate.

Sodium carbonate.	Nil.	0.050.	0.075.	0.100.	0.125.	0.150.	0.200.	0.400.
litres.								
0-10	0.980	1.493	1.449	1.613	1.493	1.667	1.429	1.695
10-20	1.031	1.316	1.538	1.493	1.613	1.667	1.587	1.852
20-30	0.800	1.053	1.370	1.471	1.515	1.724	1.613	1.538
30-40	0.602	1.042	1.266	1.493	1.538	1.538	1.408	1.111
40-50	0.532	0.971	1.124	1.282	1.587	1.587	1.087	0.807

The volume of hydrogen absorbed per increment of time declines steadily in the absence of sodium carbonate, but the decline becomes less marked until, at the optimum concentration (0.125-0.15 grm.), the action is represented by an almost linear absorption-time relation, of the type which we have previously shown to be characteristic for the hydrogenation of organic compounds in the liquid state in presence of nickel.

We have obtained further evidence of this transition from a curvilinear to linear absorption-time relation, by studying the hydrogenation of phenol at varying pressures of hydrogen in absence of sodium carbonate, and in presence of the optimum amount of this salt (0.15 grm. Na_2CO_3 for 0.5 grm. nickel).

Experiments were conducted with 100 grm. of the same sample of phenol throughout at 180° C , and at pressures of 20, 40, 60, and 80 lb. per square inch. Since, at the reaction temperature, the vapour pressure of phenol is one atmosphere, the effective, or partial, pressure of the hydrogen was approximately that indicated by the gauge, but this is only a rough approximation, since the vapour-pressure of the products (cyclohexanol b.p. 160° C , cyclohexanone b.p. 166° C) is greater than one atmosphere at 180° C .

We give, in tabular form, the "constants" for a unimolecular action, calculated with respect to the amount of unchanged phenol present, together with the mean rates of absorption of hydrogen in litres per minute over the same intervals (successive 10-litre periods of absorption).

(i) Phenol Alone—Mean Rate of Absorption per Minute.

Pressure (lbs. per sq. in.).	40.	60.	80.
Hydrogen absorbed (litres).			
10	0.704	0.962	1.235
20	0.662	0.901	1.205
30	0.541	0.813	1.111
40	0.413	0.658	1.042
50	0.400	0.476	1.020

(i) Phenol Alone—Constants for Unimolecular Action.

Pressure (lbs. per sq. in.).	40.	60.	80.
Hydrogen absorbed (litres).			
10	0.0043	0.0060	0.0076
20	0.0046	0.0062	0.0081
30	0.0046	0.0065	0.0087
40	0.0046	0.0067	0.0094
50	0.0047	0.0067	0.0105

(ii) Phenol in Presence of Sodium Carbonate—Mean Rate of Absorption per Minute.

Pressure (lbs. per sq. in.).	20.	40.	60.	80.
Hydrogen absorbed (litres).				
10	0.347	1.042	1.449	1.852
20	0.360	0.807	1.429	2.083
30	0.299	0.820	1.408	1.818
40	0.292	0.787	1.408	2.000
50	0.219	0.763	1.316	1.754
60	—	0.714	1.087	1.515
70	—	0.538	0.781	1.087

(ii) Phenol in Presence of Sodium Carbonate—Constants for Unimolecular Action.

Pressure (lbs. per sq. in.).	20.	40.	60.	80.
Hydrogen absorbed (litres).				
10	0.0021	0.0064	0.0090	0.0114
20	0.0024	0.0061	0.0096	0.0131
30	0.0024	0.0064	0.0105	0.0140
40	0.0027	0.0070	0.0116	0.0160
50	0.0028	0.0079	0.0132	0.0179
60	—	0.0093	0.0153	0.0209
70	—	0.0123	0.0200	0.0271

The figures for phenol alone at the lower pressures give perfectly sound constants for a "unimolecular" action with respect to the phenol present, a result which we previously obtained* in the case of other phenolic compounds (iso-eugenol and coumarin) at atmospheric pressure, and which is indicative of catalyst poisoning induced by the organic compound. In presence of sodium carbonate, the experimental data are no longer expressed by a logarithmic curve, and the action is more nearly represented by a linear relation.

The transformation of a "logarithmic" into a "linear" type of action by means of the addition of the "promoter" sodium carbonate is, when taken in conjunction with our previous work, strong evidence that the action of the carbonate is a protective one with respect to the catalyst, rendering the latter free to exercise its normal function. At the same time, and in agreement with this evidence, the relation which we have established between the concentrations of carbonate and catalyst (p. 23) indicates that the amount of protective agent must be in proportion to the amount of catalyst present in order to effect the maximum acceleration.

At high pressures in absence of sodium carbonate the unimolecular "constant" also increases steadily, a result which indicates that the acceleration in rate due to hydrogen concentration is not accompanied by any increase in the rate of poisoning of the catalyst by the phenol; in other words, the catalyst has not time to get thoroughly poisoned before it has finished its work of hydrogenation.

Furthermore, the fact that unimolecular constants are produced in the other cases indicates that the poisoning effect is slow enough to be measured, and that it is a function of the amount of phenol present; and, combined with the foregoing observation, may be supposed to suggest that the actual toxicity is caused by an *association of too stable a nature* between the nickel and phenol or some product of the latter (one simple possibility is that the retardation is due to formation of nickel phenate).

We may add that the data obtained for hydrogenation of phenol at various pressures indicate that the influence of pressure is very similar to that on the hydrogenation of other oxygenated compounds;† the closest resemblance is found in such cases as the hydrogenation of citral or of carvone. Thus phenol behaves like other oxygenated compounds containing a number of centres of unsaturation open to hydrogenation.

Whilst we have not been able to state in detail the action of sodium carbonate in the hydrogenation of phenol, the results are of interest, in the

* 'Roy. Soc. Proc.,' A, vol. 98, pp. 27-40 (1920).

† 'Roy. Soc. Proc.,' A, vol. 100, p. 248 (1921).

present state of vagueness on the subject of "promoters," because they establish for one particular case—

- (i) The connection between optimum concentration of promoter and amount of *catalyst*, not of organic compound;
- (ii) The transformation of the action from one typical of the presence of catalyst poisons (in absence of carbonate) to one almost of the usual type prevailing in the absence of any catalyst poison (in presence of carbonate);
- (iii) The "acceleration" of the action in presence of the "promoter" is in this case not a true acceleration, but the removal of a retardation; this leaves the catalyst itself free to behave more normally.

A Study of Catalytic Actions at Solid Surfaces. Part IX.—The Action of Copper in Promoting the Activity of Nickel Catalyst.

By E. F. ARMSTRONG, D.Sc., F.R.S., and T. P. HILDITCH, D.Sc.

(Received June 7, 1922.)

One of the most interesting cases of promoter action is that in which a mixture of two substances, each of which functions as a catalyst for the same action, shows greater activity than either constituent alone.

Thus in the synthesis of ammonia an iron-molybdenum catalyst is stated to afford greater yields of ammonia than is given by either of the metals alone.* Again, the production of formaldehyde from methyl alcohol and air was found by Hochstetter to be more effectively performed in presence of a silver-copper alloy than by either silver or copper alone.† Carbon monoxide is oxidised more efficiently in presence of certain mixtures of oxides, for example "hopcalite," than in presence of the constituent oxides (manganese and copper oxides).‡

A somewhat different case concerns the simultaneous action of two catalysts exerting different functions.

Camphor can be converted to camphane by catalytic reduction over nickel to borneol, dehydration of the latter to camphene over alumina, and hydrogenation of camphene to camphane. The hydrogenation proceeds readily at or below 200° C., but the dehydration in presence of alumina takes place at 350° C. or

* 'Badische Anilin und Soda Fabrik,' German Patent No. 5833 (1911).

† U.S.A. Patents 1100076, 1110289.

‡ Lamb, Bray and Frazer, 'J. Ind. Eng. Chem.,' vol. 12, p. 213 (1920).